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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁵ : C04B 41/60, 41/65	A1	(11) International Publication Number: WO 93/12052 (43) International Publication Date: 24 June 1993 (24.06.93)
(21) International Application Number: PCT/GB92/02345 (22) International Filing Date: 17 December 1992 (17.12.92) (30) Priority data: 9126899.5 19 December 1991 (19.12.91) GB (71) Applicant (for all designated States except US): ASTON MATERIAL SERVICES LIMITED [GB/GB]; Aston Science Park, Love Lane, Aston Triangle, Birmingham B7 4BJ (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): PAGE, Christopher, Lyndon [GB/GB]; Aston Material Services Limited, Aston Science Park, Love Lane, Aston Triangle, Birmingham B7 4BJ (GB).		(74) Agent: BARKER, BRETTELL & DUNCAN; 138 Hagley Road, Edgbaston, Birmingham B16 9PW (GB). (81) Designated States: AT, AU, BB, BG, BR, CA, CH, CS, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, UA, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: IMPROVEMENTS IN AND RELATING TO TREATMENTS FOR CONCRETE (57) Abstract This invention relates to a method of inhibiting alkali-silica or alkali-aggregate reactions (AAR/ASR) in concrete structures by introducing lithium compounds or the like in conjunction with conventional techniques for the treatment of steel reinforcement corrosion. It is also proposed to provide lithium compounds in repair concretes, grouts or mortars and use the difference in concentration between the article under repair and the repair material to introduce the lithium ions into the concrete under repair, once again inhibiting AAR/ASR reactions.		

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IMPROVEMENTS IN AND RELATING TO
TREATMENTS FOR CONCRETE

It is known that concretes which contain certain forms of siliceous aggregate are prone to generate expansive reaction products (alkali-silica gel) if sufficient concentrations of sodium, potassium and hydroxyl ions are present in the concrete pore liquid. This phenomenon, known as alkali-aggregate reaction (AAR) or alkali-silica reaction (ASR), can give rise to deleterious expansion and cracking of the concrete.

It has already been proposed to use lithium compounds as a means of inhibiting AAR/ASR in concretes which contain potentially reactive aggregates.

What we now propose is the introduction into, or presence of lithium ions (or the like), in hardened concrete in conjunction with specific techniques of reinforcement corrosion control or concrete repair so that the lithium ions are conveyed to local sites within the concrete where AAR/ASR is most likely to be initiated. Alternatively the lithium compounds may be introduced during the manufacture of a concrete article when using a reinforcing technique. Thus we primarily intend to use lithium ions in solutions, slurries or admixtures for treatment of existing concrete structures, but lithium ions, or the like, could be deliberately provided in the original concrete in anticipation of some form of subsequent treatment of steel reinforcement corrosion.

A number of techniques that are used for the treatment of steel reinforcement corrosion in concrete structures can cause localised enhancement of the concentrations of sodium, potassium and hydroxyl ions

in the concrete pore liquid, thereby increasing the risk of expansion and cracking due to AAR/ASR in concretes that contain susceptible aggregates. (Such corrosion treatment techniques include cathodic protection, electrochemical desalination, electrochemical realkalisation, and patch repair with cementitious mortar, grout or concrete).

The invention is concerned with the application of lithium compounds in conjunction with the aforementioned techniques for the treatment of steel reinforcement corrosion, with the aim of inhibiting or preventing AAR/ASR from arising as a deleterious side-effect. The effectiveness of lithium compounds as a means of inhibiting or arresting AAR/ASR in concretes which contain potentially reactive aggregates is thought to depend on the formation at the aggregate surface of an insoluble lithium silicate which has little tendency to expand in the presence of water.

According to a first aspect the invention comprises the use of lithium (or the like) compounds as inhibitors of alkali-aggregate/alkali-silica reactions in reinforced concrete subjected to cathodic protection, electrochemical desalination, electrochemical realkalisation, or patch repair treatments.

According to a second aspect the invention consists in a method of reducing AAR/ASR in concrete which is reinforced comprising the steps of providing mobile lithium ions in the concrete, and passing an electrical current through the concrete and/or reinforcement.

According to a third aspect the invention consists in a method of producing reinforced or prestressed concrete comprising the steps of providing metal reinforcing within the concrete, providing mobile lithium ions in or on the concrete, and ensuring that an electrical current is applied to the concrete and/or reinforcing.

In this way lithium ions may conveniently be introduced to a structure during its construction so that they are present if an electric current is passed at any stage during the life of a concrete structure.

Preferably the methods comprise arranging for the lithium ions to be conveyed to specific local sites within the concrete. The concrete thus has regions of high lithium concentration and regions of low lithium concentration.

According to a fourth aspect the invention consists in applying to concrete a chemical which contains a substance which migrates in an electric field through the concrete and which is attracted to regions of the concrete where AAR/ASR are likely to occur, and which preferentially reacts at said regions to form an insoluble second substance which does not expand substantially in the presence of water.

According to a fifth aspect the invention consists in a method of repairing concrete structures by applying repair substances which incorporate lithium compounds to the concrete structure so that lithium ions diffuse into substrate concrete adjacent to areas subject to repair so as to inhibit AAR/ASR in the substrate concrete.

According to a sixth aspect the invention comprises a concrete article or structure having regions of high concentration of lithium ions (or the like) and/or regions of low concentrations of lithium ions (or the like).

Preferably the high concentration of lithium ions is present in close proximity to the sites where AAR/ASR is prevalent.

Applications of the invention will now be described by way of example only.

Example 1

Cathodic Protection of Reinforced Concrete

Cathodic protection is applied to reinforcing steel by passing electrical current between it and an extended anode system attached to the surface of the concrete. The reinforcement acts as the cathode of an electrolytic cell. The anode system may take a variety of forms such as a metallic mesh coated with a cementitious overlay, a conductive paint, a sprayed metal coating, or a conductive asphalt overlay.

The current is normally supplied continuously for the remaining service-life of the structure by means of a variable D.C. power source. The latter may be adjusted from time to time to provide a sustained level of polarisation of the steel reinforcement which is judged to be appropriate on the basis of monitoring relative to reference electrodes at various positions.

Whilst the overall average current density applied to a structure can be controlled (typical specified

values being less than 20mA/m^2), the current distribution to the reinforcement cannot be made entirely uniform and, in practice, local areas of the embedded steel often receive substantially higher than average current densities.

The cathodic processes which take place on the surface of the reinforcing steel, particularly in the areas of enhanced local current density, generate high local concentrations of sodium, potassium and hydroxyl ions thus increasing the risk of AAR/ASR in the vicinity of the steel. This risk may be reduced if lithium compounds (such as lithium hydroxide, lithium nitrite, lithium acetate, lithium benzoate etc) are introduced at or near the surface anode system because the positively charged Li^+ ions will migrate under the influence of the applied electrical field towards the steel cathode. Electromigration of Li^+ will tend to occur preferentially to areas of steel where the local cathodic current density is highest and where the greatest risk of AAR/ASR, therefore, exists.

Convenient ways of introducing the lithium compounds, at appropriate concentrations, will differ somewhat for different anode systems. In the cases of the metallic mesh/cementitious overlay type of anode system, incorporation of the lithium compound as an admixture in the cementitious overlay is often practicable. In the cases of conductive paint, sprayed metal, or conductive asphalt anode systems, the absorption of a solution of the lithium compound into the pre-dried concrete surface prior to the application of the anode coating would be practicable and, in certain applications, the provision of "drip-feed" mechanisms for introducing further lithium-containing solution beneath the surface anode would be possible.

Other ways of introducing the lithium compounds include pumping them into the concrete.

The appropriate concentration for a system will vary for different concretes, and should preferably be determined by small scale tests. A concentration of greater than 0.1M in a cementitious overlay is believed to be suitable in some cases, although this figure may vary considerably. We would normally envisage using a concentration of less than 2M, but of course small scale tests could be used to indicate the appropriate range of suitable concentrations.

Example 2

Electrochemical Desalination and Realkalisation of Reinforced Concrete

Electrochemical desalination and realkalisation treatments applied to reinforced concrete are essentially similar to cathodic protection in that they involve the passage of a current between the steel reinforcement cathode and an anode mounted on the surface of the concrete. The anode is normally a metallic mesh, which is placed in an electrolyte (often in the form of a slurry with wood fibre pulp) in contact with the concrete surface. The main difference between these treatments and cathodic protection, as normally applied, is that they involve the passage of much larger current densities (circa 1A/m^2) for shorter times (usually no longer than a few months in total). The cathodic processes which take place on the surface of the reinforcing steel again generate high local concentrations of sodium, potassium and hydroxyl ions thus enhancing the risk of AAR/ASR in the vicinity of the steel. The introduction of lithium compounds

(such as lithium hydroxide, lithium nitrite, lithium acetate, lithium benzoate or other soluble lithium compounds) into the electrolyte surrounding the anode and/or the concrete provides a simple and convenient method of reducing this risk because positively charged Li^+ ions will migrate rapidly under the influence of the applied electrical field towards the steel cathode, as in the case of cathodic protection.

As previously mentioned it is believed that the lithium ions react preferentially with the siliceous aggregate to give an insoluble lithium silicate at the aggregate surface which does not expand anything like as much as an alkali-silica gel in an alkali-silica reaction.

Since the introduction of lithium (and any other mobile ions) tends to reduce the transport number of chloride ions, the time required for effective electrolytic desalination of reinforced concrete structures may be increased somewhat when lithium-based electrolytes are employed as described above. Small scale trials can be used to ascertain whether this is likely to cause practical difficulties in the cases of particular structures. In circumstances where it appears that treatment times will be extended to an inconvenient degree, it can be advantageous to carry out electrolytic desalination as a two stage process with water and an aqueous solution containing lithium ions as the external electrolytes in the anode slurry for the two stages.

Example 3

Patch Repairs with Cementitious Mortars, Grouts and Concretes

Concrete structures which have become cracked, either as a consequence of reinforcement corrosion or by other means, such as mechanical damage, are often repaired by removing the loose (or otherwise suspect) material and patching the affected regions with cementitious mortars, concretes etc. In cases where the repair material contains higher concentrations of alkalis (i.e. sodium, potassium and hydroxyl ions) than the substrate concrete, diffusion of these alkalis from the repair into the surrounding concrete will occur. This leads to an enhanced risk of AAR/ASR occurring around the repaired region in cases where the substrate concrete contains susceptible aggregates.

This risk may be conveniently reduced by the incorporation into the repair material of controlled quantities of lithium compounds (such as lithium hydroxide, lithium nitrite, lithium acetate, lithium benzoate etc) as admixtures. The concentration of Li^+ in the pore solution of the cementitious repair material must be sufficient to ensure that its diffusion into the surrounding substrate concrete is rapid relative to the rates of diffusion of Na^+ and K^+ from the repair material. The anions associated with the lithium compounds used must not be of sorts (eg. Cl^- , SO_4^- etc) that are likely to cause any deleterious effects on the durability of the repair material or the surrounding concrete or its reinforcement. It may be advantageous to employ lithium compounds in which the anion (e.g. hydroxide, nitrite, benzoate, acetate etc) functions as an inhibitor of steel corrosion since this provides enhanced protection to the steel reinforcement in the vicinity of the repairs.

As for any admixtures, it is necessary to establish the effects of the lithium compounds on basic properties (eg workability, setting and hardening characteristics etc) by preliminary tests with the cementitious repair materials to be used for particular patch repairs.

CLAIMS

1. A method of inhibiting alkali-aggregate or alkali-silica reactions in concrete characterised in that it comprises the steps of introducing a substance into the concrete and causing the substance to migrate within the concrete, the substance inhibiting alkali-aggregate or alkali-silica reactions.

2. A method according to Claim 1 characterised in that the substance is caused to migrate preferentially to areas highly susceptible to alkali-aggregate or alkali-silica reactions.

3. A method according to Claim 1 or Claim 2 characterised in that the substance migrates due to the presence of a concentration differential.

4. A method according to Claim 1 or Claim 2 characterised in that the substance migrates due to the presence of an electric field.

5. A method according to Claim 4 characterised in that the electric field is applied as a function of reinforcement corrosion control.

6. A method according to any preceding Claim characterised in that the substance which migrates reacts with aggregates present in the concrete to form a second substance.

7. A method according to Claim 6 characterised in that the second substance forms on the surface of the aggregate.

8. A method according to Claim 6 or Claim 7 characterised in that the second substance is insoluble and does not expand substantially in the presence of water.

9. A method according to any preceding Claim characterised in that the substance contains lithium ions.

10. A method according to any preceding Claim characterised in that the substance is introduced to the concrete by contacting a mixture containing the substance with a surface region of the concrete.

11. A method according to Claim 10 characterised in that the mixture is a cementitious overlay and the anode is provided in the mixture.

12. A method according to any preceding Claim characterised in that the substance is introduced to the concrete during construction.

13. A method according to any of Claims 4 to 12 characterised in that the electric field is applied a considerable period of time after the chemical is introduced.

14. A method according to any preceding Claim characterised in that the substance is present in concrete (or other material) applied by way of repair.

15. A method according to any preceding Claim characterised in that it further comprises the step of desalinating the concrete with water prior to introducing the migrating substance.

16. A reinforced concrete article characterised in that it has been treated by a method in accordance with any preceding Claim.

17. A method of producing a reinforced or prestressed concrete article characterised in that it comprises the steps of providing metal reinforcing within the concrete, providing mobile lithium ions in (or on) the concrete and applying an electric field to the article at some stage during the life of the concrete article.

18. A method of repairing a concrete article characterised in that it comprises the steps of preparing a repair mix which incorporates one or more lithium compounds and applying the repair mix to the concrete article, the concentration of lithium in the repair mix being such that lithium ions diffuse into the concrete article being repaired and inhibit alkali-silica or alkali aggregate reactions.

19. A reinforced concrete article characterised in that it has regions of high lithium ion concentration and regions of low lithium ion concentration.

20. A reinforced concrete article according to claim 19 characterised in that the concentration of the lithium ions is highest where the current density due to the applied electric field is highest.

21. A method of inhibiting alkali-aggregate or alkali-silica reactions substantially as herein described.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 92/02345

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)*

According to International Patent Classification (IPC) or to both National Classification and IPC
 Int.Cl.5 C 04 B 41/60 C 04 B 41/65

II. FIELDS SEARCHED

Minimum Documentation Searched†

Classification System

Classification Symbols

Int.Cl.5

C 04 B

Documentation Searched other than Minimum Documentation
 to the Extent that such Documents are Included in the Fields Searched‡

III. DOCUMENTS CONSIDERED TO BE RELEVANT*

Category °	Citation of Document, †† with indication, where appropriate, of the relevant passages ‡‡	Relevant to Claim No. ‡‡
X	EP,A,0312387 (NISSAN CHEMICAL INDUSTRIES LTD) 19 April 1989, see page 1, line 52 - page 2, line 44; claims 1,3	1-3, 6-10, 12, 16
Y	---	4-5, 11, 13, 15, 17
P, Y	EP,A,0499437 (ICI AMERICAS INC.) 19 August 1992, see abstract; claims 1-5; page 2, lines 4-48; page 3, lines 40-45; examples 1-5 --- ---	4-5, 13, 17

* Special categories of cited documents: †‡

"A" document defining the general state of the art which is not considered to be of particular relevance

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IV. CERTIFICATION

Date of the Actual Completion of the International Search

30-03-1993

Date of Mailing of this International Search Report

28. 04. 93

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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No. *
4 Y	EP,A,0398117 (O. VENNESLAND) 22 November 1990, see abstract; claims 1,19; column 3, line 24 - column 5, line 58; column 9, lines 6-57 ----	11
4 Y	US,A,5039556 (J.A. COGLIANO et al.) 13 August 1991, see abstract; claims 1,4-6 ----	15
6 X	Chemical Abstracts, vol. 106, no. 26, June 1987, (Columbus, Ohio, US), see page 310, abstract no. 218671y, & JP,A,61256951 (NISSAN CHEMICAL IND., LTD) 14 November 1986, see abstract ----	1-3,6-9 12,16
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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

GB 9202345

SA 68469

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 13/04/93. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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